

An artificial model of photosynthetic photosystem II: visible-light-derived O₂ production from water by a di-μ-oxo-bridged manganese dimer as an oxygen evolving center†

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Visible-light-derived O₂ production was yielded by conjugating water oxidation catalysis by [(OH₂)(terpy)Mn(μ-O)₂Mn(terpy)(OH₂)]³⁺ as an oxygen evolving center model and photo-sensitization of [Ru(bpy)₃]²⁺ as a photoexcitation center model at an interlayer of mica.

Light absorption of the chlorophyll photoexcitation center so-called P₆₈₀ induces electron transfer from P₆₈₀ to pheophytin as a primary electron acceptor and subsequently to two quinones at photosystem II (PS II) in photosynthesis.¹ To the formed P₆₈₀^{•+} radical cation, an electron is donated from an oxo-bridged tetra-manganese cluster so-called *oxygen evolving complex* (OEC) through a Tyr_Z residue as an electron mediator. Water oxidation to evolve O₂ occurs upon accumulating four oxidizing equivalents on OEC by the successive photo-induced electron-transfer process. Development of a functional PS II model is a challenging task in the related fields to provide mechanistic insight into photosynthetic O₂ production and shed light on the promising way towards an artificial photosynthetic model.^{2–5} The most functional OEC models capable of catalyzing water oxidation to O₂ have been synthesized based on ruthenium and iridium complexes.^{6–13} Synthetic manganese-oxo complexes reported as a functional OEC model are few, though OEC is composed of oxo-bridged manganese clusters.^{14–18} The extension of manganese-oxo complex-based OEC models to a photochemical system is expected to yield a strikingly similar PS II model.

We previously reported that [(OH₂)(terpy)Mn(μ-O)₂Mn(terpy)(OH₂)]³⁺ (**1**) (terpy = 2,2':6',2''-terpyridine) works as a catalyst for water oxidation when it is adsorbed on layer compounds of kaolin, montmorillonite and mica.^{15,19} This encourages us to develop a functional PS II model using the layer compound/**1** adsorbate as an OEC model. It is well-defined that with a metal-to-ligand charge transfer (MLCT) photoexcited state of [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) it is thermodynamically possible to split water to O₂ and H₂.

Herein we report that visible-light-derived O₂ production is yielded by conjugating water oxidation catalysis by **1** and photo-sensitization of [Ru(bpy)₃]²⁺ at an interlayer of mica.

Mica is able to adsorb cationic **1** and [Ru(bpy)₃]²⁺ by cation exchange with Na⁺ (cation exchange capacity: CEC = 1.2 meq g⁻¹). **1** was adsorbed onto mica from an aqueous solution of **1**, followed by similar adsorption of [Ru(bpy)₃]²⁺ to yield the mica adsorbate of **1** and [Ru(bpy)₃]²⁺ (mica/**1**/[Ru(bpy)₃]²⁺). The X-ray diffraction (XRD) data indicate that either **1** or [Ru(bpy)₃]²⁺ is intercalated into an interspace between mica layers (Fig. S1, ESI†). For the diffuse reflectance (DR) spectra of the mica/**1**/[Ru(bpy)₃]²⁺ adsorbate, the absorption at λ_{max} = 475 nm assigned to MLCT transition of [Ru(bpy)₃]²⁺ was 5.2 times more intense than that for the mica/[Ru(bpy)₃]²⁺ adsorbate with the identical [Ru(bpy)₃]²⁺ concentration (w_{Ru} = 20 μmol g⁻¹) (Fig. S2†). The specifically intense absorption of the mica/**1**/[Ru(bpy)₃]²⁺ adsorbate can be explained by localization of [Ru(bpy)₃]²⁺ close to the mica surface. This means that [Ru(bpy)₃]²⁺ is shallowly-intercalated outside **1** in an interlayer of mica.

The mica/**1**/[Ru(bpy)₃]²⁺ adsorbate (3.3 μmol **1**, 0.4 μmol [Ru(bpy)₃]²⁺, 20 mg mica) was suspended in an acetate buffer solution (pH = 6.2, 2.0 ml) containing 15 mM S₂O₈²⁻. When visible light (λ > 420 nm) irradiated the suspension with stirring, O₂ was significantly evolved, as shown in Fig. 1a. In the absence of a component of **1**, [Ru(bpy)₃]²⁺ and S₂O₈²⁻, O₂ was not evolved (Fig. 1b–e), showing that these three components are essential for the photoinduced O₂ evolution. Nor was O₂ evolved in the homogeneous solution containing the same amounts of **1**, [Ru(bpy)₃]²⁺ and S₂O₈²⁻ (Fig. 1f). This result suggests that **1** and [Ru(bpy)₃]²⁺ adsorbed on mica are effective for O₂ evolution, which is consistent with the conclusion for a chemical water oxidation system.¹⁹ 5.5 μmol of O₂ was evolved by light irradiation of the suspension (pH = 6.2, 2.0 ml) containing the mica/**1**/[Ru(bpy)₃]²⁺ adsorbate for 17 h under the conditions (1.6 μmol (164 μmol g⁻¹) **1**, 0.25 μmol (25 μmol g⁻¹) [Ru(bpy)₃]²⁺, 10 mg mica, 15 mM S₂O₈²⁻). The turnover numbers (TN) of **1** and [Ru(bpy)₃]²⁺ were 3.4 and 88 during the 17 h catalysis, respectively. This result corroborates that **1** and [Ru(bpy)₃]²⁺ works as a catalyst and a photocatalyst in photochemical water oxidation, respectively, because the TN numbers are more than unity. Nevertheless, TN of **1** is considerably lower compared with TN = 15–17 for a chemical water oxidation system.¹⁹ Instability of [Ru(bpy)₃]²⁺ is supposed to be responsible for the lower TN of **1**. Most likely, [Ru(bpy)₃]²⁺ might be decomposed by oxidized **1** during the photochemical reaction.

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† Electronic supplementary information (ESI) available: Experimental details, X-ray diffraction (XRD) spectroscopic data of mica adsorbate, UV-visible diffuse reflectance (DR) spectroscopic data of mica adsorbates, electron-impact-ionization mass spectra (EI-MS) in ¹⁸O-labeling experiments, kinetic data of photochemical O₂ evolution. See DOI: 10.1039/c0cc03114c

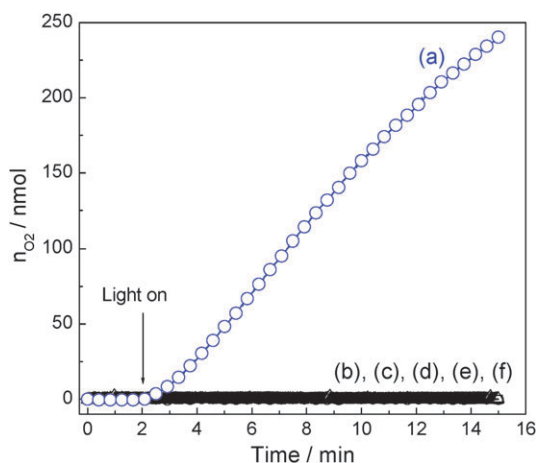


Fig. 1 Time courses of the amount ($n_{\text{O}_2}/\text{mol}$) of O_2 evolved in photochemical water oxidation in an aqueous suspension (2.0 ml, pH = 6.2) of 0.2 M acetate buffer and 15 mM $\text{S}_2\text{O}_8^{2-}$ (a) containing the mica/ $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbate, (b) the mica/**1** adsorbate, (c) the mica/ $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbate, (d) neat mica. (mica, 20 mg; **1**, 3.3 μmol ($164 \mu\text{mol g}^{-1}$); $[\text{Ru}(\text{bpy})_3]^{2+}$, 0.4 μmol ($20 \mu\text{mol g}^{-1}$)). (e) In the absence of $\text{S}_2\text{O}_8^{2-}$ under the conditions of (a). (f) In a homogenous solution (pH = 6.2, 2.0 ml) containing 3.3 μmol (1.6 mM) **1** and 0.4 μmol (0.2 mM) $[\text{Ru}(\text{bpy})_3]^{2+}$ and 15 mM $\text{S}_2\text{O}_8^{2-}$.

In order to identify an oxygen atom source for O_2 evolution, ^{18}O -isotope labeling experiments for photochemical water oxidation were carried out in a H_2^{18}O medium, and the evolved gas was analyzed using an electron-impact-ionization mass spectroscopic (EI-MS) technique. In a 99% H_2^{18}O medium, EI-MS spectra gave a main peak at $m/z = 36$ assigned to $^{18}\text{O}_2$ and a minor peak (4.3%) at $m/z = 34$ assigned to $^{18}\text{O}^{16}\text{O}$ in a range of $m/z = 25\text{--}40$, in contrast to a single peak at $m/z = 32$ for $^{16}\text{O}_2$ observed for the experiment in an abundant water medium (Fig. S3†). This result corroborates that the oxygen atoms in O_2 evolved are originated exclusively from water.

The initial O_2 evolution rate ($v_{\text{O}_2}/\text{mol s}^{-1}$) was given from the initial slope of the time course of the amount ($n_{\text{O}_2}/\text{mol}$) of O_2 evolved. v_{O_2} increased linearly with the light intensity and deviated downward above 95 mW cm^{-2} . This result indicates that the O_2 evolution is rate-determined by the subsequent reactions rather than the photochemical process above 95 mW cm^{-2} under the conditions employed (Fig. S4†). The following experiments were conducted under the light intensity of 127 mW cm^{-2} . The second order dependency of v_{O_2} with respect to the concentration of **1** ($w_{\text{Mn}}/\text{mol g}^{-1}$) was given (Fig. S5†), suggesting that two equivalents of **1** are required for photochemical O_2 production. This is consistent with the cooperative catalysis reported in the chemical water oxidation system.¹⁹ Although O_2 was hardly evolved below $w_{\text{Ru}} = 5 \mu\text{mol g}^{-1}$ under the constant w_{Mn} ($164 \mu\text{mol g}^{-1}$) conditions, v_{O_2} critically increased at more than $w_{\text{Ru}} = 7.5 \mu\text{mol g}^{-1}$ (Fig. S6†). Light harvesting by $[\text{Ru}(\text{bpy})_3]^{2+}$ should be an important factor to yield photochemical O_2 evolution. However, it can not explain the critical v_{O_2} increase with w_{Ru} reasonably, because the light absorption by $[\text{Ru}(\text{bpy})_3]^{2+}$ increases linearly with w_{Ru} for the mica/ $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbate.

The photoexcited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ is well-known to be sufficiently quenched by $\text{S}_2\text{O}_8^{2-}$ in a homogeneous aqueous

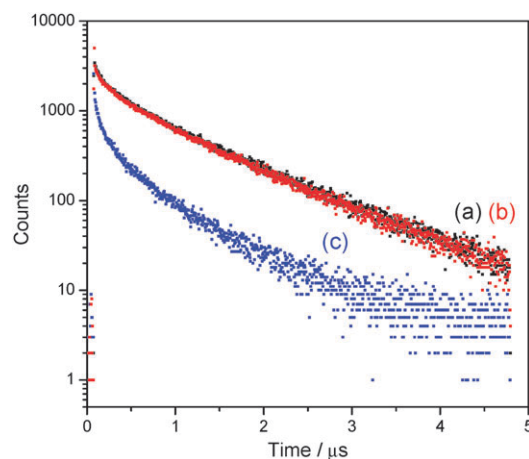


Fig. 2 Emission decays of photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ intercalated in mica in water using a single-photon counting technique. (a; black) mica/ $[\text{Ru}(\text{bpy})_3]^{2+}$, (b; red) mica/ $[\text{Ru}(\text{bpy})_3]^{2+}$ in the presence of $\text{S}_2\text{O}_8^{2-}$ in a liquid phase, (c; blue) mica/**1** (8 eq.)/ $[\text{Ru}(\text{bpy})_3]^{2+}$. 0.08 μmol ($20 \mu\text{mol g}^{-1}$) $[\text{Ru}(\text{bpy})_3]^{2+}$, 4 mg mica, acetate buffer (3.0 ml, pH = 6.2), 25 °C, Ar atmosphere.

solution. Nevertheless, the emission decay from the photoexcited state did not change if 15 mM $\text{S}_2\text{O}_8^{2-}$ is contained in an aqueous suspension of the mica/ $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbate,²⁰ showing that the photoexcited state in mica is not quenched by $\text{S}_2\text{O}_8^{2-}$ in the liquid phase (Fig. 2b). $\text{S}_2\text{O}_8^{2-}$ anions in the liquid phase can not be allowed to come close to $[\text{Ru}(\text{bpy})_3]^{2+}$ in an anionic interspace between mica layers for quenching due to electrostatic repulsion. In contrast, the emission decay is significantly fast for the mica/**1**/ $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbate, as shown in Fig. 2c. This indicates that the photoexcited state is quenched by **1** in mica. The electron transport for photochemical O_2 evolution in the mica/**1**/ $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbate is initiated from the photoexcitation of $[\text{Ru}(\text{bpy})_3]^{2+}$, followed most probably by electron transfer from **1** to the excited $[\text{Ru}(\text{bpy})_3]^{2+}$ to form oxidized **1** and $[\text{Ru}(\text{bpy})_3]^+$. The reductive quenching of the excited $[\text{Ru}(\text{bpy})_3]^{2+}$ is well-known from previous reports,^{21,22} though we do not have any spectroscopic evidence for $[\text{Ru}(\text{bpy})_3]^+$ formation yet. The successive photoinduced electron-transfer processes could generate oxidizing equivalents that are used for water oxidation catalysis. On the other hand, $[\text{Ru}(\text{bpy})_3]^+$ could be re-oxidized to $[\text{Ru}(\text{bpy})_3]^{2+}$ by $\text{S}_2\text{O}_8^{2-}$ in a liquid phase to suppress a back electron transfer from $[\text{Ru}(\text{bpy})_3]^+$ to the oxidized **1**, as reported in the literature.²³ However, since $[\text{Ru}(\text{bpy})_3]^+$ formed close to **1** in mica can not react directly with $\text{S}_2\text{O}_8^{2-}$, an electron on $[\text{Ru}(\text{bpy})_3]^+$ must be relayed to $[\text{Ru}(\text{bpy})_3]^{2+}$ close to the mica surface for the re-oxidation by $\text{S}_2\text{O}_8^{2-}$ possibly by a successive self-exchange electron-transfer reaction between $[\text{Ru}(\text{bpy})_3]^+$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ (electron hopping) in mica (Fig. 3). The electron relay by electron hopping could occur efficiently at the higher w_{Ru} conditions to achieve photochemical O_2 evolution. This could be a possible explanation for the critical v_{O_2} increase with w_{Ru} .

For preliminary experiments, photochemical O_2 production was not yielded under the same conditions ($164 \mu\text{mol g}^{-1}$ **1**, $20 \mu\text{mol g}^{-1}$ $[\text{Ru}(\text{bpy})_3]^{2+}$, 20 mg mica, 15 mM $\text{S}_2\text{O}_8^{2-}$) using two control adsorbates: (i) the mica/ $[\text{Ru}(\text{bpy})_3]^{2+}$ /**1** adsorbate

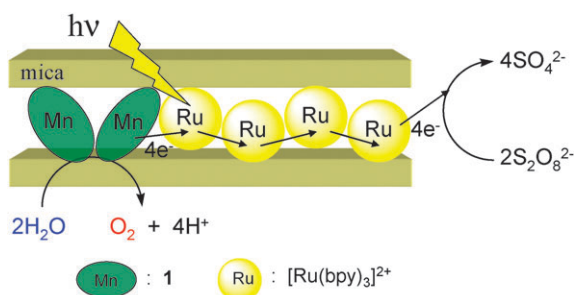


Fig. 3 Illustration of possible vectorial electron transport for photochemical O_2 production. Electrons are relayed from **1** to $[Ru(bpy)_3]^{2+}$ close to the mica surface by a successive self-exchange electron-transfer reaction between $[Ru(bpy)_3]^+$ and $[Ru(bpy)_3]^{2+}$ (electron hopping) in mica, further transferring to $S_2O_8^{2-}$ in a liquid phase.

prepared by an opposite adsorption order: $[Ru(bpy)_3]^{2+}$ followed by **1**, and (ii) the mica/ $(\mathbf{1} + [Ru(bpy)_3]^{2+})$ adsorbate prepared by co-adsorption from the mixed solution of **1** and $[Ru(bpy)_3]^{2+}$. The DR spectra for these control adsorbates did not exhibit the specifically intense absorption at 475 nm due to $[Ru(bpy)_3]^{2+}$ in contrast to the case for the mica/ $\mathbf{1}/[Ru(bpy)_3]^{2+}$ adsorbate, implying that $[Ru(bpy)_3]^{2+}$ is not shallowly-intercalated outside **1** in an interlayer for these control adsorbates (Fig. S2†). These results suggest that the arrangement of **1** and $[Ru(bpy)_3]^{2+}$ in an interlayer is important for photochemical O_2 evolution. The arrangement of inside **1** and outside $[Ru(bpy)_3]^{2+}$ could allow for efficient vectorial electron transport from **1** to $S_2O_8^{2-}$. The present work demonstrates the illustration of artificial PS II model for **1** and $[Ru(bpy)_3]^{2+}$ to act as OEC and P_{680} models, respectively. We are undertaking an advanced project to build up the artificial photosynthetic model by assembling the PS II model and a H_2 production catalyst system.

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